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**MILKING DEVICES**

The present invention relates to devices and components for milking apparatus, in particular to components of such devices such as milk extracting devices, and  
5 liners. In a particular aspect it relates to a liner comprising an improved teat receiving flexible sleeve.

**Background of the Invention**

10 Machine milking has been available for about a century. The basic construction of a milking device, which is still in use today is based on an invention patented by Gillies in 1902, and comprises a double chambered teat cup designed to operate with a pulsating vacuum. The teat cup comprises a flexible sleeve made of rubber, forming one flexible wall of a chamber, where the teat cup shell forms the other  
15 wall. In the space between the two walls a pulsating vacuum is applied whereby the sleeve will expand and contract, thereby causing a massaging action on a teat on which the teat cup has been applied.

The flexible sleeve is provided as a part of a so called teat cup liner (or inflation in  
20 US English; in the present specification and claims the term "liner" will be used throughout).

A milking apparatus as a whole comprises a number of different components, many of which currently are made of different kinds of rubber, e.g. tubing, nozzles, liners  
25 etc.

As an example, a modern teat cup system is disclosed in US-6,176,200 (Pettersen). It comprises a tubular head portion capable of receiving a teat, and a shaft portion forming an inner wall of the pulsating vacuum chamber. The shaft portion is  
30 flexible and normally made of a rubber compound.

In order to be accepted by the market, devices forming the components of milking apparatus, such as teat cups and liners, must exhibit a number of properties. Examples that can be mentioned are the following:

35 Enhanced milking performances, i.e., milk speed, milk yield, slip, strip yield

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Good teat treatment

Long lifetime of the liner and capable of functioning at the same high level over the entire lifetime.

Uniform quality of the liners.

5 Chemical and physical endurance

Easy to clean

Easy to replace

Environment friendly, e.g., recycling of the material

10 Currently available components of milking apparatus, such as liners, are most often made of rubber materials.

The product must comply with regulations relating to material and to articles and products that are intended to come into contact with foodstuff.

15

**Summary of the Invention**

20 The present invention therefore seeks to provide improved devices and components usable in milking apparatus and that meet all the requirements listed above. This is achieved in accordance with the invention by a milking device for a milking apparatus that comprises a material, selected from the group consisting of i) thermoplastic elastomers (TPE), as defined in ISO 18064, ii) plasticised PVC, iii) Vinyl TPE, and exhibiting a number of selected properties.

25 This novel device is defined in claim 1.

30 In a particular embodiment the device is a milk extracting device, i.e. a device constituting a part or component of a milking apparatus that acts on the teat of an animal, or cooperates with other parts of the milking apparatus, such that the udder will release milk in a controlled manner.

A further embodiment of the invention provides a teat contact element that is to be applied to or over the teat.

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A still further embodiment provides an improved teat cup liner. This liner comprises at least a teat receiving flexible sleeve, adapted to be positioned on/over a teat in a close fit.

5 The devices according to the invention provides the following advantages:

1. No compounding or blending of the material is required for the manufacturing process. TPE:s are like thermoplastics ready for use as delivered. TPE:s are not sensitive to storage.

10

2. Simpler processing with fewer steps is needed. TPE:s has the processing simplicity of a thermoplastic giving more efficient processing and thereby significantly lower processing costs.

15

3. Shorter fabrication cycles leading to lower energy consumption and manpower cost.

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4. Recycling of scrap material possible. Scrap resulting from thermoset production is normally discarded. As with thermoplastics regrind from TPE processing can be recycled to give same properties as virgin material.

5. Better quality control and closer tolerances on fabricated parts.

25

6. In most cases a lower density.

7. No low temperature hardening (crystallisation) as with some thermoset rubbers.

30

8. Since TPE:s are recyclable, it facilitates environmentally friendly for products made of these materials as far as recycling is concerned.

35

9. Simpler to combine different materials in one and the same unitary structure, such that different parts are made of different materials.

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10. Compositing, such as making layered structures of different materials is possible.

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Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and  
 5 modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description and the accompanying drawings which are given by way of illustration only, and thus not limitative of the present invention, and wherein

10 Fig. 1 shows an example of a prior art device for a milking apparatus, namely a teat cup and a liner; and

Fig. 2 schematically shows an embodiment of the invention in the form of a teat cup liner.

15

#### Detailed Description of Preferred Embodiments

For the purpose of this application, the expression "milking device" is taken to encompass any member, component or device usable in a milking apparatus or  
 20 system, that is to be used in the dairy business e.g. in contact with the milk, and therefore must comply with regulations relating to materials and articles intended to come into contact with foodstuffs. A non-limiting listing of examples of milking devices in this sense is tubing, nozzles, connectors, teat cups, teat cup liners, sleeves for teat cup liners. It is to be noted that said milking device may be used for animals,  
 25 e.g. cows, buffalos, sheep and goats and other ruminant animals.

In Fig. 1, an exemplary prior art teatcup is disclosed. It is provided with a teatcup liner 1 which is mounted in a teatcup shell 2. The teatcup liner 1 is essentially rotationally symmetrical with respect to a longitudinal axis 3 and comprises an upper tubular head portion 4 and a tubular, flexible teat receiving sleeve portion 5  
 30 extending downwardly from the head portion 4. The head portion 4 comprises a first upper end 6 and a second lower end 7. Beneath the upper end 6, the tubular head portion 4 comprises a lip 8 extending radially inwardly and defining an essentially circular central opening. The tubular head portion 4 forms a passage between the  
 35 first end 6 and the second end 7 to the inner space of the teatcup liner for receiving a tent. The lower end 7 comprises an annular recess 9 which is engaged by the upper

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end portion of the teatcup shell 2. The lower part of the sleeve 5 comprises a peripheral surrounding recess 10 which is engaged by the lower end portion of the teatcup shell 2. The recesses 9 and 10 are shaped in such a manner that a closed space 11 is formed between the teatcup liner and the teatcup shell 2, which space 11 forms a pulsating chamber of the teatcup. In its lower part, the teatcup liner 1 connects to prolongation pieces 12 and 13, which form a milk conduit which may be connected to a claw (not disclosed). The teatcup liner 1 is manufactured in an elastic material, for instance natural or synthetic rubber.

10 The invention is based on the finding that thermoplastic elastomers (TPE) can be made to meet the material requirements for providing devices and components for milking apparatus and systems. Therefore, a brief introduction to the TPE technology will be given.

#### 15 Thermoplastic elastomers (TPE)

##### Introduction

Before the development of TPEs there were generally speaking only rigid or semi-rigid articles products could be manufactured and processed with the new technology for thermo-plastics. The production of thermoplastics are faster, less energy consuming, cleaner and it is easier to re-use scrap.

For elastomeric materials there were lack of alternatives for thermoset rubbers. For applications not exposed to extreme temperatures there is not any fundamental need for temperature resistant crosslinking-sites. The use of thermoset rubbers will have the accompanying disadvantages of the crosslinking.

30 The incentives for developing thermoplastic materials exhibiting elastic properties without any permanent crosslinking sites have therefore been strong.

Thermoplastic elastomers (TPE) are materials that combine the processing properties of a thermoplastic material with the elastomeric properties of a rubber material.

35 Thermoplastic elastomers are two-phase systems. One of the phases is a hard polymer that gives the mechanical strength at service temperatures but becomes

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fluid when heated above the melting- or transition temperature. The other phase is a soft rubbery polymer.

There are principally two ways to achieve the properties; block copolymers or polymer blends.

Block copolymers meeting the definition of thermoplastic elastomers consist of two phases one hard and one soft, formed from segments in the same chain of a molecule. The harder segment could be crystalline with a high melting temperature or an amorphous material with a high glass transition temperature. The soft segment is always amorphous with a very low glass transition temperature.

Examples: TPS (amorphous hard phase), TPU, TEEE, TPA (semicrystalline hard phase). Abbreviations see below.

TPE made from polymer blends, are blends of a hard material, almost exclusively semi-crystalline with a high melting temperature in a continuous phase blended with a softer at least mainly amorphous material with a very low glass-transition temperature.

Examples: TPO, TPV

#### Nomenclature

According to ISO 18064 the classes and abbreviations for TPE:s are (within bracket other common abbreviations):

TPE: Thermoplastic elastomers in general.

TPS: (SBC) Polystyren/elastomer block copolymers.

TPO: Polypropylene/ EP copolymers blends.

TPV: Thermoplastic vulcanisates.

TPU: Polyurethane block copolymers.

TEEE (COPE) Polyester block copolymers.

TPA: (COPA) Polyamide block copolymers.

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**General Properties of TPE-materials**

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| <b>Table 1. Comparison of General Properties for TPE Materials</b> |         |          |         |         |         |         |
|--|---------|----------|---------|---------|---------|---------|
|  | TPS     | TPO      | TPV     | TPU     | TEEE    | TPA     |
| Density (kg/dm <sup>3</sup> )                                      | 0.9-1.1 | 0.89-1.0 | 0.9-1.0 | 1.1-1.3 | 1.1-1.3 | 1.0-1.2 |
| Shore Hardness   | 3A-60D  | 60A-75D  | 35A-50D | 60A-85D | 90A-72D | 60A-75D |
| Low temperature limit °C   | -70     | -60      | -60     | -70     | -65     | -40     |
| High temperature limit (continuous) °C                             | 120     | 120      | 135     | 120     | 125     | 170     |
| Compression set resistance at 100°C                                | F       | P        | G       | F/G     | F       | F/G     |
| Resistance to hydrocarbon fluids                                   | F/G     | P        | G/E     | F/E     | G/E     | G/E     |
| Resistance to aqueous fluids                                       | G/E     | G/E      | G/E     | F/G     | P/G     | F/G     |
| Price ratios   | 1-3.6   | 1.5-2.5  | 2.5-3.0 | 2.0-4.0 | 4.0-6.0 | 4.0-9.0 |
| P=Poor F=Fair G=Good E=Excellent                                   |         |          |         |         |         |         |

**Styrenic Block copolymers (TPS or SBC)**

5

TPS materials include three distinctly different main types:

- Styrene-butadiene-styrene block copolymers (SBS)
- Styrene-isoprene-styrene block copolymers (SIS)
- styrene-ethylene-butylene-styrene block copolymers (SEBS)

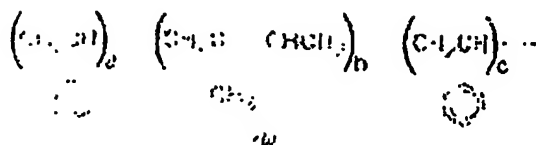
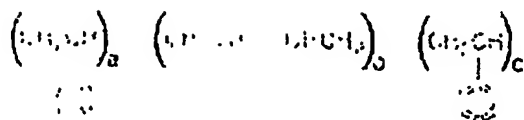
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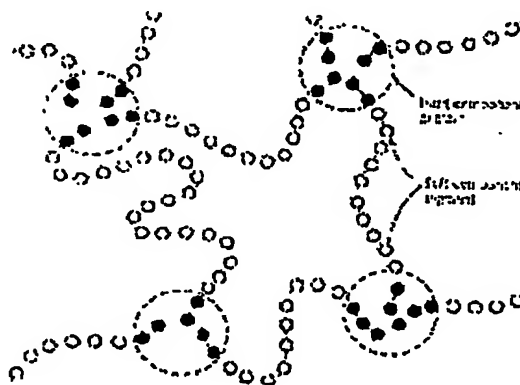
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**SBS and SIS polymers**

- 5 Styrene and butadiene (or isoprene) are incompatible and form a two-phase system with two distinct  $T_g$ 's. The stiffer styrene-phase acts as physical crosslinking points between the more flexible butadiene (or isoprene) phase.



10

**Morphology of TPS-polymers**

The polymers are made by anionic polymerisation working principally like following.

15 An alkyl-Lithium initiator can be used, reacting with styrene monomer;  $R + Li^+ + n S \rightarrow R-(S_n)-Li^+$ . This product can be called a "living polymer" and it can initiate further polymerisation step when adding butadiene (or isoprene)  $R-(S_n)-Li^+ + x B \rightarrow R-(S_n)-(B_x)-Li^+$ . Finally adding styrene monomer and eventually terminating agent gives  $R-(S_n)-(B_x)-(S_{n2})-R_2$ .

Only styrene, butadiene and isoprene among suitable monomers are easily polymerised with this method, so only SBS and SIS are directly produced on commercial scale. Both polymers contain, however, double bonds in the elastomeric segments. These bonds are reactive and limit the stability of the product.

SEBS is therefore produced by hydrogenation of SBS. The butadiene segment in the hydrogenated product is a random mixture of 1,4- and 1,2- isomers. The resulting product in the elastomeric segment is essentially a copolymer of ethylene and butylene, thereby the name SEBS.

Melt viscosities of TPS are very high compared to the related homopolymers. This is one of the reasons that TPS, contrary to other TPE:s almost always is used in compounds with the TPS-polymer content less than 50%.

#### Properties:

The block structure creates the unique properties of these polymers. The hard styrene segments form hard spherical domains, linked by elastomeric segments. The hardness of the material depends on the ratio between PS and the elastomer. In general the higher the content of polystyrene the harder will the product be.

**Table 2. Comparison TPS grades**

| TPS-type/ property   | SBS  | SIS       | SEBS                      |
|----------------------|--|-----------|---------------------------|
| Relative stiffness   | 1  | 0,5       | 2                         |
| Relative cost        | 1  | 1,3       | 2                         |
| Stability            | Moderate   | Moderate  | Excellent                 |
| Typical end-products | Footwear   | Adhesives | automotive parts<br>cable |
| TPS Strong points    | Cheap, hardness down to Shore A 30. Temperature range -50-120°C, easily coloured, resistance to fatigue and abrasion, approvals for food contact, transparency possible, low density, resistance against polar fluids and water. |           |                           |
| TPS weak points      | High compression set, low chemical resistance against oils, fuels and organic solvents.  |           |                           |

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Huvudföres Krossen

**Thermoplastic Olefins TPO:s**

Thermoplastic olefins are blends of polypropylene (PP) and ethylene-propylene copolymer (EPM) or ethylene-propylene-diene polymer (EPDM). The term EP(D)M covers both EPDM and EPM.

PP-EP(D)M blends are produced by intensive mixing of PP and EPDM and/or EPM.

After mixture there is a two-phase structure. The polypropylene has a tendency to form a continuous phase even when the PP-content is below 50%. This might be due to it's lower viscosity. At higher EP(D)M levels, above 70%, a two co-continuous phase may occur.

The polypropylene is normally an isotactic homopolymer or an isotactic PP with minor content of ethylene. The melting point of these semi-crystalline polymers are in the range 145-165°C.

A TPO can therefore retain many of it's mechanical properties at high temperatures. An EP(D)M with 50:50 ratio ethylene and propylene are almost completely amorphous although both polyethylene and polypropylene are semicrystalline polymer. Changing i.e. the ethylene content to a higher ratio gives some crystallinity. The net effect of a small amount of ethylene crystallinity greatly influences the strength of the rubber. Therefore a EP(D)M with an high amount of ethylene content seems to most preferred.

**Properties:**

Since PP and EP(D)M can be blended in any ratio, there is theoretically a continuous spectrum from lightly modified thermoplastic PP to EP(D)M reinforced with thermoplastic.

**Table 3. Comparison TPO-grades**

| Property/ TPO | EP(D)M/PP<br>80/20 | EP(D)M/PP<br>67:33 | EP(D)M/PP<br>50/50 |
|---------------|--------------------|--------------------|--------------------|
|               |                    |                    |                    |

|                        |  |        |        |
|------------------------|--|--------|--------|
| Tensile strength (Mpa) | 6  | 9,5    | 12     |
| Shore A Hardness       | 77   | 87     | 95     |
| Brittle point          | <-60°C   | <-60°C | <-60°C |
| TPO Strong points      | Service temperature range -60-125°C, low brittle point, high impact strength, High E-modulus.<br>Good resistance to polar organic fluids.              |        |        |
| TPO weak points        | Low elasticity, low elongation at break, high compression set.<br>Poor resistance to hydrocarbons and halocarbons.<br>Drying needed before processing. |        |        |

### Polymers based on metallocene technology

During the 90's new polyolefinic resin based on metallocene catalyst technology were introduced. These are copolymers, consisting of ethylene and higher olefins such as 1-octene. The metallocene technology makes it possible to design very precisely the distribution of e.g. 1-octene and ethylene in the polymer chain. When the 1-octene content is around 30% or more there is no crystallinity in the polymer. If some crystallinity is desired a polymer with lower amount of 1-octene can be produced.

Dow Dupont has launched the Engage-polymer which they classify as a POE, polyolefinic elastomer. Exxon Chemicals version is the Exact-range. Exxon prefer however to designate their products "plastomers".

In TPO:s they can replace the EP(D)M content in a PP/ EP(D)M system. They can give better processibility than EPDM, and improved impact strength.

These polymers can also be used as sole polymer. To achieve acceptable properties as a thermoplastic they need then to have some crystallinity, and thereby a 1-octene content not more than 30%. Although having elastomeric properties they are not considered to be a true TPE-material but a thermoplastic material. (Compare flexible PVC below).

These POE:s or plastomers may also be crosslinked using silane, peroxide or radiation technology. They are then competing with thermoset rubbers like EPDM.

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Int. t. Patent (de) reg.verket

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**Thermoplastic Vulcanisates (TPV)**

Hans-Joachim Kassen

Thermoplastic vulcanisates (TPV) are two-phase systems consisting of a thermoplastic continuous phase and a crosslinked rubber as the discontinuous phase. The dominating system is PP/EPDM but there are also PP/NBR systems.

The rubber phase is highly vulcanised in contrast to TPO:s where the rubbery phase is just partly or not vulcanised. The vulcanisation of the rubber phase results in numerous property improvements.

**Table 4. Comparison of a TPV and a TPO of the same base formulation**

|  | Unvulcanised<br>(TPO) | Vulcanised<br>(TPV) |
|--|-----------------------|---------------------|
| Ultimate Tensile strength (psi)  | 583                   | 1984                |
| Ultimate elongation (%)  | 630                   | 430                 |
| 100% modulus (psi)   | 412                   | 725                 |
| Compression set (%)  | 78                    | 31                  |
| Tension set (%)  | 52                    | 14                  |
| Swell in ASTM oil No 3 (%)   | 162                   | 52                  |
| Shore A hardness   | 81                    | 84                  |
| Formulation: EPDM 91.2 PP 54.4 Extender oil 36.4 carbon black 36.4 (parts by weight) |                       |                     |

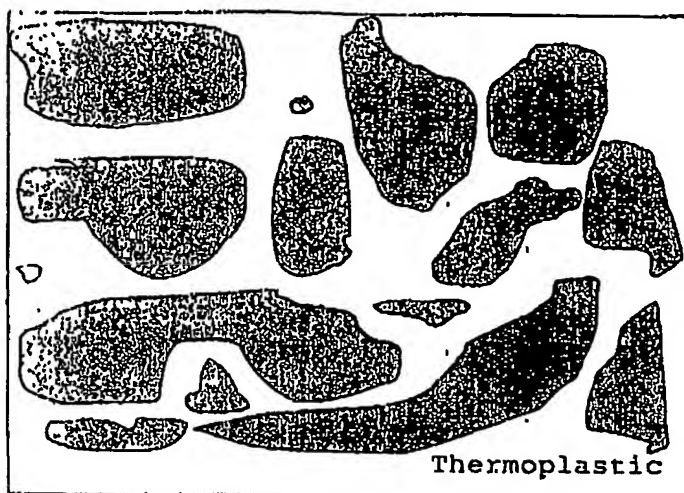
The dynamic vulcanisation means melt mixing under shear of a thermoplastic material and a soft elastomer with simultaneous vulcanisation of the latter. The temperature must be high enough to melt the thermoplastic and induce the curing reaction in the elastomer. It is important that the mixing takes place during the entire vulcanisation step so that there will be no continuous phase of EPDM formed and thereby a resulting thermoset material.

The rubber-like properties and the thermoplastic processibility of TPV depends directly on the morphology. To achieve optimum properties the crosslinked rubber particles should have an average particle size of 1-2  $\mu\text{m}$ . The degree of crosslinking in the dispersed particles is of course also of importance.

Pat. 1. Patent- og registreret

2002 12 20

Inventor: Dr. Brann



#### 5 Morphology in a thermoplastic vulcanizate

It is essential to have good contact between the two phases although separated. If the interfacial tension is too large, incorporation of compatibilisers may be necessary.

**Table 5. Properties of a PP-EPDM TPV:s of different hardnesses**

| Shore A                           | 35A   | 55A   | 80A   |
|-----------------------------------|-------|-------|-------|
| Tensile Strength (Mpa)            | 2     | 5     | 12    |
| Elongation at break (%)           | 320   | 380   | 520   |
| Brittle point (°C)                | < -60 | < -60 | < -60 |
| Compression set 168h at 100°C (%) |       | 28    | 44    |
| Swell IRM-oil 903 (%)             | 108   | 69    | 37    |
| Heating 135°C 30 days:            |       |       |       |
| Retention elongation at break     | 122%  | 99%   | 73%   |
| Change Shore A (units)            | -1    | +7    | +2    |

|                             |   |
|-----------------------------|---|
| TPV (PP-EPDM) strong points | - Dielectric properties,- Excellent flex fatigue resistance,- Excellent ozone resistance, heat-ageing resistance, low density |
| TPV (PP-EPDM) weak points   | Limited resistance against hydrocarbons, although better than TPO   |

The most well-known TPV-grades are the Santoprene-grades from Advanced Elastomer System (AES). But also the Sarlink-grades from DSM are well established.

- 5 A growing potential for TPE:s are overmoulding thermoplastics, to give materials with rigid mechanical properties, but with a soft touch. Polyolefinic TPV:s has a potential problem due to their poor affinity to other materials. To overcome this both Santoprene and Sarlink-grades have been developed which have good affinity to polyamide.

10

Thermoplastic vulcanisates of PP and NBR is used when there is a need of better resistance against hydrocarbons. The NBR rubber has much better oil resistance than EPDM. AES manufactures such TPVs with the trade name Geolast.

- 15 Another way to improve the oil resistance is to use polyacrylate as the elastomer in TPV. This has been utilised by Optatech, Finland with the trade name Pacrel.  
**Thermoplastic Polyurethane Elastomers (TPU)**

- 20 TPUs are block copolymers with urethane backbone linkages. They are synthesised by condensation of diisocyanates with short chain diols and polyester and /or polyether diols.

- 25 The short-chain diols along with diisocyanates form the the crystalline hard phase in the TPU. The crystallites acts as physical crosslinking points and heat resistance of TPUs are closely related to the melting point of these crystallites. Short chain diols like 1,4- butanediol and 1,6- hexanediol are commonly used.

- 30 The soft segment is formed from hydroxylterminated polyesters or hydroxyl-terminated polyethers.

The soft segment of TPU will determine the elastic and low-temperature properties.  
The hardness and modulus will be determined by ratio of hard and soft segments.

**Table 6. Comparison of TPU materials**

| <i>TPU with polyether soft block</i> | <i>TPU with polyester soft block</i>   |
|--------------------------------------|--|
| Higher resilience                    | Greater tear strength                  |
| Hydrolytic stability                 | Greater abrasion resistance            |
| Low temperature flexibility          | Greater toughness                      |
| Microbial resistance                 | Greater resistance to non-polar fluids |

|                   |  |
|-------------------|--|
| TPU strong points | High abrasion and tear resistance.<br>No plasticiser.<br>Excellent resistance to mineral oils (diesel) and greases.<br>Excellent resistance to non-polar solvents. |
| TPU weak points   | Limited resistance against aromatic chlorinated and polar solvents.<br>Not available at softness below Shore A 70.<br>Long-term temperature limited to 80°C.       |

5

**Thermoplastic Copolyesters (TEEE), (COPE)**

Consists of block copolymers of alternating hard and soft segments connected by ester and ether linkages. the soft segments can be polyethers, polyesters or copolyesters. The principal differences between the soft segments are the same as for TPUs. The hard segment is almost exclusively polybutylterephthalate (PBT)

10

A comparison of different TEEE materials from DSM Engineering Plastics, with PBT as the hard segment and three different soft segments a polyetherester (PTMG) Arnitel E, a polyether (PPG) Arnitel P and a polyesterester Arnitel U showed following:

15



**Table 7. Properties of Arnitel TEEE-materials**

|  | Arnitel E<br>PBT-polyetherester | Arnitel P<br>PBT-polyether | Arnitel U<br>PBT-copolyester |
|--|---------------------------------|----------------------------|------------------------------|
| Elasticity   | o                               | o                          | +                            |
| Low-temperature<br>resistance                        | o                               | o                          | -                            |
| Elongation at break                                  | o                               | --                         | -                            |
| Tear strength  | o                               | -                          | +                            |
| Abrasion resistance                                  | o                               | -                          | ++                           |
| Flex Fatigue   | o                               | o                          | o                            |
| Continuous use<br>temperature                        | 120                             | 120                        | 150                          |
| Ageing properties                                    |                                 |                            |                              |
| Oxidative  | o                               | o                          | +++                          |
| UV   | o                               | o                          | ++                           |
| Hydrolysis   | +                               | o                          | -                            |
| Water uptake   | o                               | -                          | +                            |
| Colour   | o                               | o                          | +                            |
| ++ excellent + good o acceptable - poor -- very poor |                                 |                            |                              |

|                    |  |
|--------------------|--|
| TEEE strong points | Mechanical strength<br>Elasticity<br>Dynamic properties<br>Impact resistance<br>Heat resistance<br>Service temperature -60 to + 150°C<br>Chemical resistance |
| TEEE weak points   | Not available at hardness lower than 35 Shore D.   |

**Polyamide block Copolymers (TPA, COPA)**

Block copolymers of hard and soft segments. The hard segments are polyamides and soft segments are polyolblocks with a polyether chain or a polyester chain.

The polyamide block can be any PA 6, PA6/6, PA 11, PA12, PA 6/11 or PA 6/12.

5 This will determine the melting point and influence the density and the chemical resistance.

10 The type of soft segment will influence properties like resilience, tear strength, hydrolytic stability, abrasion resistance, low temperature flexibility, toughness and microbial resistance non-polar solvents like.

Polyether chain are most common and are preferred for their low temperature resistance and hydrolytic stability. Polyester chains are preferred when good solvent resistance and high temperature stability is preferred. (See tables for PU).

15

| Table 8. TPA materials |  |
|------------------------|--|
| TPA strong points      | High mechanical strength<br>Heat resistance<br>Tear strength<br>Fatigue resistance<br>Abrasion resistance<br>Chemical resistance |
| TPA weak points        | Susceptible to hydrolysis  |

#### Other Materials with TPE-properties

##### Plasticised PVC

20

There is actually one material that is classified as a thermoplastic but actually has properties similar to TPE. Plasticised polyvinyl chloride (PVC) commonly regarded as a amorphous thermoplastic material can be used more than 100°C above it's glass-transition temperature, still keeping acceptable mechanical properties.

25

Although not in nomenclature regarded as a TPE, plasticised PVC (=flexible PVC or pPVC) was in fact the first material to combine elastomeric properties with

thermoplastic processing. Nowadays it is known that this is due to that the polyvinyl chloride chain partly gives regular crystal-like structures involving two or more chains giving melttable crosslinking points. These structures have a very wide range of melting temperatures, from below 0°C up to almost 200°C. The upper temperature limit for PVC with standard plasticiser is around 60°C, and with speciality plasticiser 105-120°C.

There is a number of plasticisers that can be used for PVC. The standard plasticiser is DOP di-octylphthalate or more correctly DEHP (di-ethylhexylphthalate). Due to environmental reasons the plasticisers is now replaced with other phthalates with higher molecular weight. For specific purposes, like high heat resistance trimellitates is used, or DUP (di undecyl-phthalates). For low-temperature resistance adipates such as DIDA is used, for non-migrating and chemical resistance purposes, polymeric plasticisers based on polyesters are preferred.

The compression set properties, are especially at elevated temperatures poor. This is due to that new crystal-like structures will be created in the compressed form during the testing and thereby hold the sample in it's compressed shape.

Plasticised PVC has had a tremendous success in competition with rubbers in new or established products. For decades plasticised PVC was the only alternative to rubber. PVC is cheaper than thermoset rubbers and processed much more efficiently.

#### Vinyl TPE:s

Conventional plasticised PVC is based on plasticisers who have a very good miscibility with the PVC. When mixing with elastomers like NBR or acrylate elastomers a two-phase system more like i.e. the TPO and TPV:s can be achieved. Such materials can especially give better compression set and better chemical resistance than conventional plasticised PVC.

The suppliers of these materials sometimes call them Vinyl TPE:s, although there seems to be doubtful that these material are generally accepted as a member of the TPE family. As described above normal plasticised PVC could also be described as a TPE.

Hydro Polymers has developed the Vaycron series "vinyl TPEs" which can give compression set down to 25% at 70°C.

**Table 9. Comparison of "Vinyl TPE" Vaycron LCS with plasticised PVC and EPDM**

|                      | Vaycron LCS | Flexible PVC | EPDM |
|----------------------|-------------|--------------|------|
| Compression set      | 1-2         | 3            | 1    |
| Processability       | 1           | 1            | 3    |
| Adhesion             | 1           | 1            | 3    |
| Colourability        | 1-3         | 1            | 3    |
| Surface finish       | 1           | 1            | 3    |
| Low-temp flexibility | 1-2         | 3            | 1    |
| Recyclability        | 1           | 1            | 3    |
| Cost                 | 2           | 1            | 2-3  |

Ranking 1=best 2=intermediate 3 lowest/worse

- 5 The American producer Teknor Apex introduced a range of TPE:s based on PVC alloys based on PVC with ultra high molecular weight. They have still better elastomeric properties and can give compression set properties similar to TPV:s. These vinyl TPE:s are soft and show a combination of low compression set and good oil resistance.

**Table 10. Comparison of PVC-TPE with other TPE:s and flexible PVC**

|  | PVC-TPE | TPV  | SEBS | TPO  | Flexible PVC |
|--|---------|------|------|------|--------------|
| Hardness Shore A                       | 55      | 55   | 55   | 55   | 55           |
| Density                                | 1.11    | 0.97 | 0.91 | 0.96 | 1.14         |
| Tensile strength (MPa)                 | 7.1     | 3.9  | 8.5  | 3.0  | 10.3         |
| Compression set after 22 h at 70°C (%) | 41      | 34   | 42   | 67   | 70           |
| Elongation (%)                         | 310     | 330  | 790  | 330  | 390          |

|  |      |     |     |             |      |
|--|------|-----|-----|-------------|------|
| Elongation retention after ageing in ASTM oil No 1 3 days at 125°C | 104% | 23% | 91% | falls apart | 35%  |
| Swelling in ASTM oil No 1 3 days at 125°C                          | -10% | 42% | 34% | falls apart | -15% |

In a newsletter from spring 2002 Teknor Apex announced that they are developing vinyl TPE:s with POE:s as flexible component giving materials with very good low temperature properties and superior heat ageing resistance.

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Another approach to give PVC elastomeric properties is adding elastomers in the PVC-polymerisation process. PVC will graft to the elastomers during the polymerisation. Vinnolit, Germany has two grades, Vinnolit VK 710 where polybutyl acrylate is the elastomer and Vinnolit VK 801 where EVA is the elastomer, both in 50/50 ratio. They may be used processed alone (with appropriate additives) or used as a migration-resistant plasticisers in PVC.

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| Table 12. Some Properties important for liners |     |     |     |     |      |     |
|--|-----|-----|-----|-----|------|-----|
|  | TPS | TPO | TPV | TPU | TEEE | TPA |
| Resistance to wash temperature 90°C            | E   | E   | E   | G/E | P/G  | P/G |
| Resistance to alkali / acid                    | P   | G   | E   | F/G | F/G  | G   |
| Resistance to ozone                            | E   | E   | E   | E   | E    | E   |
| Resistance to UV                               | G   | G   | F/G | F/G | F/G  | G/E |
| Resistance to permanent deformation.           | F   | P   | G   | F/G | F    | F/G |
| Tear resistance                                | F   | F/G | G   | E   | E    | E   |
| Fatigue  | G   | P   | E   | G   | G    | G   |
| Colourability                                  | yes | Yes | Yes | yes | yes  | Yes |
| Mould to tight tolerances                      | G   | G   | E   | F/E | E    | E   |
| Elasticity                                     | F   | P   | G   | G   | G    | G   |
| P= Poor F= Fair G= Good E= Excellent           |     |     |     |     |      |     |

15 Vinyl TPE is one another type of material that could be of interest for liner application. Using a vinyl TPE with low compression set could possibly be an alternative. It would like TPV fulfil most requirements well. The Vinyl TPE:s are

reasonably priced. It is for me not clear if the compression set and fatigue resistance can match TPV, but otherwise they should well challenge TPV in chemical resistance, UV- and ozone resistance, tear strength etc.

- 5 Thus, in accordance with the invention, a milking device, as defined previously, is made of a material including one or more materials selected from a group of materials including the above discussed.

- 10 In a particular embodiment the device is a milk extracting device, i.e. a device constituting a part or component of a milking apparatus that acts on the teat of an animal, or cooperates with other parts of the milking apparatus, such that the udder will release milk in a controlled manner.

- 15 A further embodiment of the invention provides a teat contact element that is to be applied to or over the teat.

- A still further embodiment provides an improved teat cup liner. This liner comprises at least a (flexible) teat receiving sleeve, adapted to be positioned on/over a teat in a close fit.

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- In a particular embodiment of the present invention, there is provided a teat cup liner wherein it is specifically the flexible teat receiving sleeve portion of the liner that is made of such a material or material combination. A liner 20 is schematically illustrated in Fig. 2. It comprises a head portion 22, a flexible sleeve portion 24 for receiving a teat 25 in a substantially close fit. The sleeve extends from the head portion 22 to a transition region where a milk tube 26 connects to the sleeve 24. This milk tube 26 can be integrated with the sleeve or, as in the prior art device in Fig. 1, be a separate member connectable to the sleeve.

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- 30 The most important element of a liner is the flexible sleeve 24, in the sense that it is this element that performs the function, i.e. causes the udder to release the milk by a massaging action, in combination with the teat cup and the pulsating vacuum applied. Thus, in order that the liner be able to fulfil its technical function, at least the flexible sleeve must meet certain criteria with respect to material properties.

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Thus, the following are examples of properties that a liner having a flexible sleeve based on TPE, and that is connectable to the teat/animal and to the overall milking system should exhibit.

- It must be capable to remove milk from the udder of an animal by means of vacuum means
  - It should be capable of transporting milk within closed systems
  - It should be connectable via an interface to the overall milking system
  - The teat should be subjected to massage
  - A flexible sleeve that could stimulate the animal
  - The flexible sleeve should comply with regulations relating to materials and articles intended to come into contact with foodstuffs
  - The flexible sleeve should be able to act as a barrier and should not be influenced by the milk
  - A flexible sleeve that should have a tension or compression being constant or variable
  - It should exhibit a scaling function
  - A flexible sleeve that could be attached to the teat automatically or manually
  - The flexible sleeves functionality could be controlled
  - A flexible sleeve based on a material that should withstand the milking environment
  - A flexible sleeve based on a material that should be processable
  - A flexible sleeve that could be fixed and sealed against an outer hard shell
  - A flexible sleeve that could fit teats of all sizes
  - Preferably the flexible sleeve that could consist of one or many material or combinations thereof
  - A flexible sleeve based on a material that consists of TPE or TPE in combination with other materials
  - Smooth milk-transport should be allowed
- 30 The above criteria are met with a liner having a flexible sleeve made of a material that comprises a TPE, as defined in ISO 18064, or a plasticised PVC, or a Vinyl TPE, or combinations thereof, or combinations with other suitable materials.

23

Patent No. 2 0

2001-10-20

Patent No. 2 0

The elastomeric material of the milking device according to the invention, should exhibit (at least) the following properties:

- A hardness between 25 shore A and 50 shore D
- A Young's modulus between 0.1 MPa and 50 MPa
- 5 - A tensile strength typically above 0.5 MPa
- A minimum elongation of 50% without breakage

Optionally the milking device should exhibit

- A service temperature typically between -60C and +200C

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Suitably the material is resistant to acids, in particular formic acid, propionic acid, peracetic acid, and  $H_2O_2$ . The material is also preferably resistant to alkali, in particular to ammonia, NaOH and KOH.

- 15 The material should also be resistant to chlorine, ozone and to UV irradiation and thermal oxidation.

In preferred embodiments, the material exhibits a tear strength between 5 and 50 kN/m, preferably 15-35 kN/m.

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In preferred embodiments, the material exhibits a tensile strength of 0.5-40 MPa, preferably 5-20 MPa.

- 25 It should also in preferred embodiment exhibit an elongation which is more than 200% before breakage, preferably more than 300%.

- 30 The material is preferably a thermoplastic vulcanisate (TPV), comprising two phases consisting of a thermoplastic continuous phase and a cross-linked rubber as a discontinuous phase, wherein the thermoplastic elastomer comprises a binder rubber selected from silicone, EPDM, nitrile rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, halo-butyl rubber, ethylene-propylene rubber, polyisoprene, polychloroprene, polybuten copolymers, chlorosulfonated polyethylene, NBR, optionally grafted with acrylates, anhydrides.



Int. Patent-adv. reg. no.

24

2002-10-20

Hauptanmeldung

The thermoplastic elastomer preferably also comprises a crystalline polyolefin selected from polyethylene (HDPE, LDPE or LLDPE), polypropylene, or mixtures thereof, for example copolymers. By virtue of the excellent processability of the materials selected in accordance with the invention, it becomes possible to tailor  
5 liners to a large number of different applications or needs within the field of automated milking. Thus, it is possible to manufacture liners in a simple molding process to high dimensional accuracy, while combining different materials in different parts of the product. E.g. it is possible to provide the head portion and milk tube with a higher rigidity than the flexible sleeve has.

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Int. Patent class. no. 12

2007-12-20

Inventor: Dr. Brann

## CLAIMS:

1. A milking device, characterized in that at least a part thereof comprises  
5 a material, selected from the group consisting of i) thermo-plastic elastomers, as  
defined in ISO 18064, ii) plasticised PVC, iii) Vinyl TPE, said material exhibiting the  
following properties:
- 10 a) a hardness between 25 shore A and 50 shore D;  
b) a Young's modulus between 0.1 MPa and 50 MPa;  
c) a tensile strength above 0.5 MPa; and  
d) a minimum elongation of 50% without breakage.
2. A device as claimed in claim 1, exhibiting a service temperature between  
15 -60 and +200°C.
3. A device as claimed in claim 1 or 2, wherein said material is resistant to  
acids.
- 20 4. A device as claimed in claim 3, wherein the material is resistant to formic  
acid, propionic acid, peracetic acid, and H<sub>2</sub>O<sub>2</sub>.
5. A device as claimed in any preceding claim, wherein said material  
further is resistant to alkali.
- 25 6. A device as claimed in claim 5, wherein said material is resistant to  
ammonia, NaOH, and KOH.
7. A device as claimed in any preceding claim, wherein said material  
30 further is resistant to chlorine, ozone and to UV irradiation and thermal oxidation.
8. A device as claimed in any preceding claim, wherein said material  
exhibits a tear strength between 5 and 50 kN/m, preferably 15-35 kN/m.

9. A device as claimed in any preceding claim, wherein the tensile strength is 0.5-40 MPa, preferably 5-20 MPa.

10. A device as claimed in any preceding claim, wherein the elongation is more than 200% before breakage, preferably more than 300%.

11. A device as claimed in any preceding claim, wherein the material is a thermoplastic vulcanisate (TPV), comprising two phases consisting of a thermoplastic continuous phase and a cross-linked rubber as a discontinuous phase.

12. A device as claimed in claim 11, wherein the thermoplastic elastomer comprises a binder rubber selected from silicone, EPDM, nitrile rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, halo-butyl rubber, ethylene-propylene rubber, polyisoprene, polychloroprene, polybutene copolymers, chlorosulfonated polyethylene, NBR, optionally grafted with acrylates, anhydrides.

13. A device as claimed in claim 11 or 12, wherein the thermoplastic elastomer comprises a crystalline polyolefin that can be selected from polyethylene (HDPE, LDPE or LLDPE), polypropylene, or mixtures thereof, for example copolymers.

14. A device as claimed in any preceding claim, wherein the milking device is a milk extracting device.

15. A device as claimed in any of claims 1-13, wherein the milking device is a teat contact element that is to be applied to or over the teat.

16. A device as claimed in claim 15, wherein said teat contact element is a flexible sleeve (24).

17. A device as claimed in any of claims 1-13, wherein the milking device is a teat cup liner, comprising at least a teat receiving flexible sleeve, adapted to be positioned on/over a teat in a close fit.

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2000-12-20

Hans-Joachim Krosch

18. A device as claimed in claim 17, wherein the liner comprises a head portion (22), a sleeve (24) and a milk tube (26) integrated in a unitary structure.
19. A device as claimed in claim 17, wherein the liner comprises a head  
5 portion (22), a sleeve (24) and a separate milk tube (26), connectable with the sleeve (24).

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## ABSTRACT

The present invention relates to devices and components for milking apparatus, in particular to milk extracting devices. Especially it relates to components of such devices such as liners (20). The novel devices comprise a material, selected from the group consisting of thermo-plastic elastomers, as defined in ISO 18064, plasticised PVC, Vinyl TPE, said material exhibiting the following properties: a hardness between 25 shore A and 50 shore D; a Young's modulus between 0.1 MPa and 50 MPa; a tensile strength above 0.5 MPa; and a minimum elongation of 50% without breakage.

(Fig. 2)

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Patented in Sweden

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FIG. 1

FIG. 1

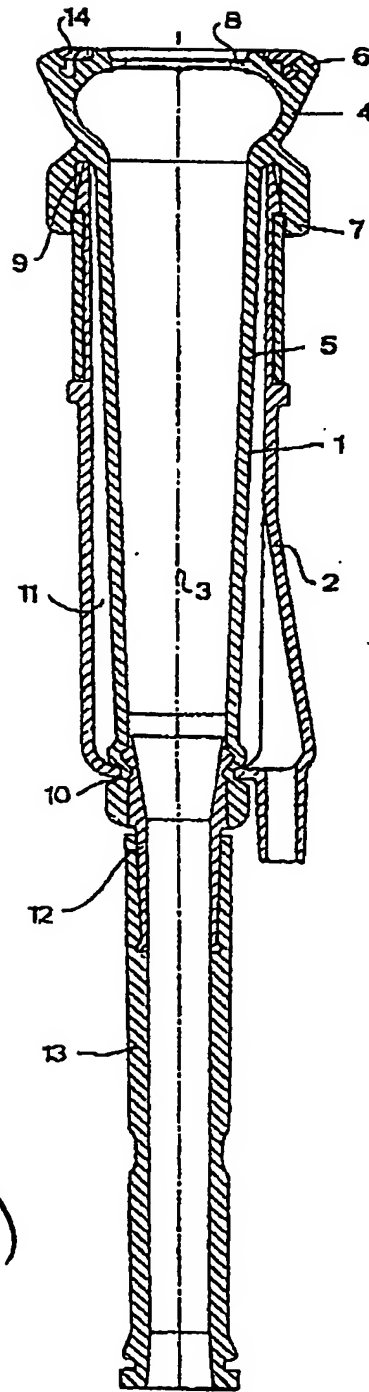


Fig. 1  
(PRIOR ART)

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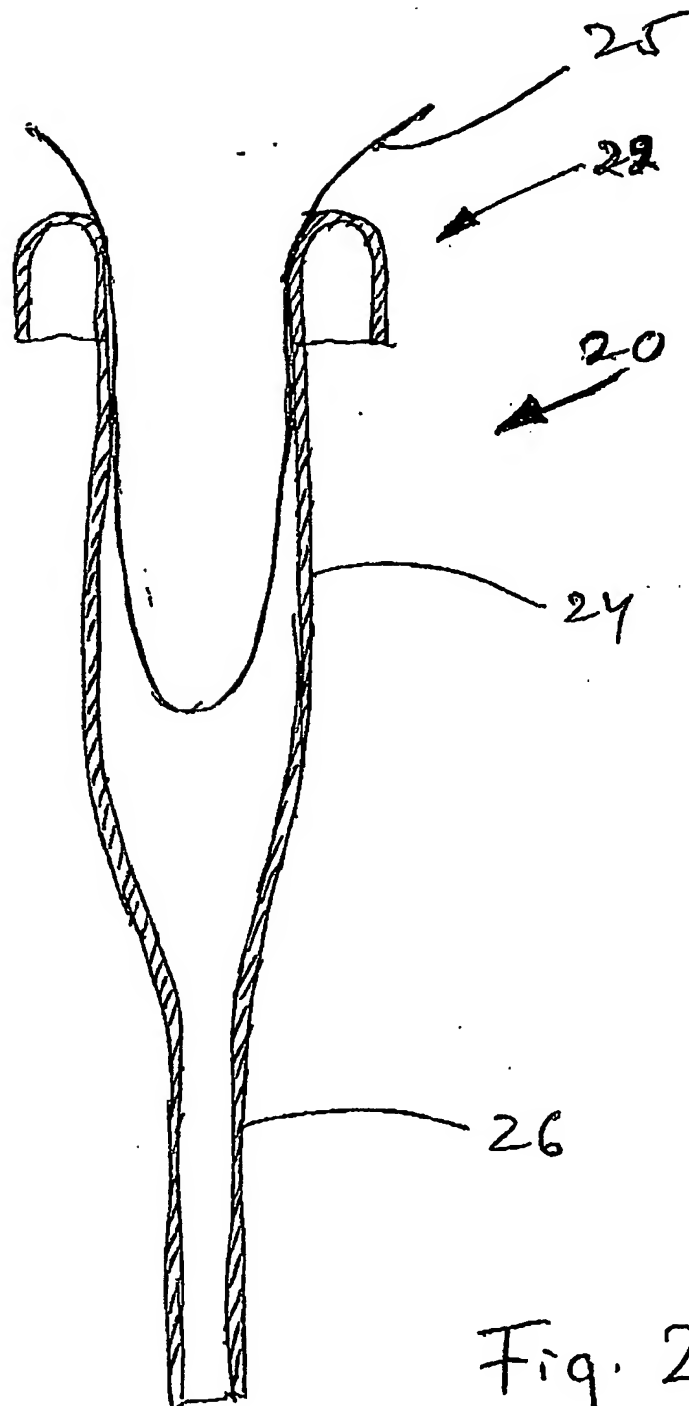


Fig. 2